Supporting Information

Catalytic Oxidation of Aromatic Hydrocarbons by a Molecular Iron-NHC Complex

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Content

1. Gas chromatography parameters

Table S4: Experimental parameters of gas chromatography analyses-

Oven Temperature / °C	**Ramp / °C/min**	**Hold / min**
***p*-Xylene Oxidation (GC-FID)** CP-Chirasil-Dex CB (0.25 μm; 25 m × 0.25 mm), He flow: 1.0 mL/min		
60	-	5
100	10	2
150	40	1
TMB Oxidation (GC-FID) Optima 5-Amine (1.50 μm; 30 m × 0.32 mm), He flow: 1.5 mL/min		
60	-	5
250	8	-
320	20	4
GC-MS VF-200ms (1.50 μm; 30 m × 0.32 mm), He flow: 2.0 psi/min, Saturn 2200 ion trap, 70 eV		
60	-	5
250	8	-
260	20	6

2. Catalytic data of *p*-xylene oxidation

Table S1. Catalytic oxidation of *p*-xylene with **1** and H_2O_2.

Entry	Cat. / pXy / H_2O_2	c(pXy) / M	T / °C	C(pXy) / % [a]	Yield / % [a]		
					2,5-DMP	2,4-DMP	DMBQ
1	1/100/10	0.5	0	5.3	2.8	2.5	0.0
2	1/100/50	0.5	0	16.7	6.3	6.6	3.8
3	1/100/75	0.5	0	22.9	7.8	8.9	6.2
4	1/100/100	0.5	0	28.1	9.1	10.6	8.4
[a] Conversion and yield were determined after 60 min by GC-FID analysis (wt.%)							

Table S2. Influence of acid and base additives on the catalytic oxidation of *p*-xylene with **1** and hydrogen peroxide. Reaction conditions: pXy (0.5 mmol), **1** (0.005 mmol, 1 mol%), H_2O_2 (50 wt% in H_2O, 0.125 mmol, 0.25 equiv.), additive (0.5 mmol, 1.0 equiv.), CH_3CN (1 mL), 0 °C, 60 min.

Entry	Additive	C(pXy) / % [a]	Yield / % [a]		Ratio 2,5-DMP/2,4-DMP
			2,5-DMP	2,4-DMP	
1	-	11.6	4.9	4.9	1.00
2	acetic acid	10.8	4.4	4.4	1.00
3	benzoic acid	10.2	4.5	3.9	1.15
4	propionic acid	10.9	4.5	4.4	1.02
5	pyridine	0.0	0.0	0.0	-
6	DMAP	0.0	0.0	0.0	-
7	NEt_3	0.0	0.0	0.0	-
8	KO^tBu	0.0	0.0	0.0	-
[a] Conversion and yield were determined after 60 min by GC-FID analysis (wt.%)					

3. Catalytic data of pseudocumene oxidation

Table S3. Catalytic oxidation of TMB catalyzed by **1** and H_2O_2.

Entry	Catalyst	Substrate	Cat/Substrate/H_2O_2	c(Substrate) / M	T / °C	C(TMB) / %[a]	Y(TMBQ) / %[a]	S(TMBQ) / %
1	**1**	TMB	1/100/50	0.5	0	29.2	4.4	15.1
2	**1**	TMB	1/100/130	0.5	0	63.1	8.9	14.1
3	**1**	TMB	1/100/150	0.5	0	70.1	9.2	13.2
4	**1**	TMB	1/100/200	0.5	0	72.5	8.7	12.1
5	**1**	TMB	1/100/300	0.5	0	61.8	6.2	10.0
6	**1**	TMB	0.3/100/100	0.5	0	34.9	3.5	10.2
7	**1**	TMB	0.5/100/100	0.5	0	49.5	5.9	11.9
8	**1**	TMB	1.5/100/100	0.5	0	53.7	6.8	12.6
9	**1**	TMB	2/100/100	0.5	0	54.6	6.6	12.1
10	**1**	TMB	4/100/100	0.5	0	56.7	6.7	11.9
11	$FeCl_2$	TMB	1/100/100	0.5	0	2.0	0.3	14.3
12	$FeCl_3$	TMB	1/100/100	0.5	0	1.8	0.2	11.1
13	**1**	2,3,5-TMP	1/100/100	0.5	0	77.3	25.9	26.1
14	**1**	2,3,6-TMP	1/100/100	0.5	0	72.9	35.0	35.3

[a] Conversion and yield were determined after 120 min by GC-FID analysis (wt.%)

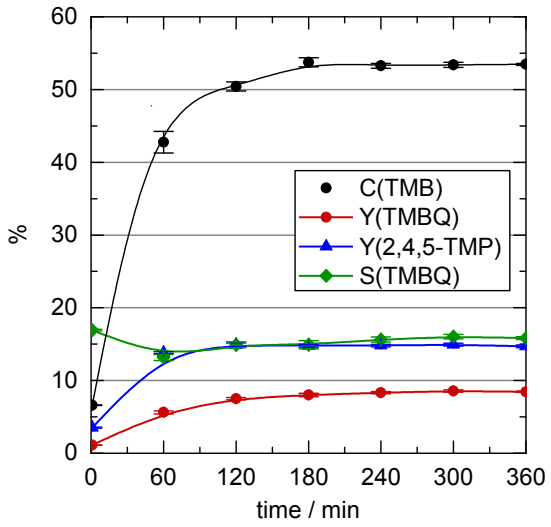
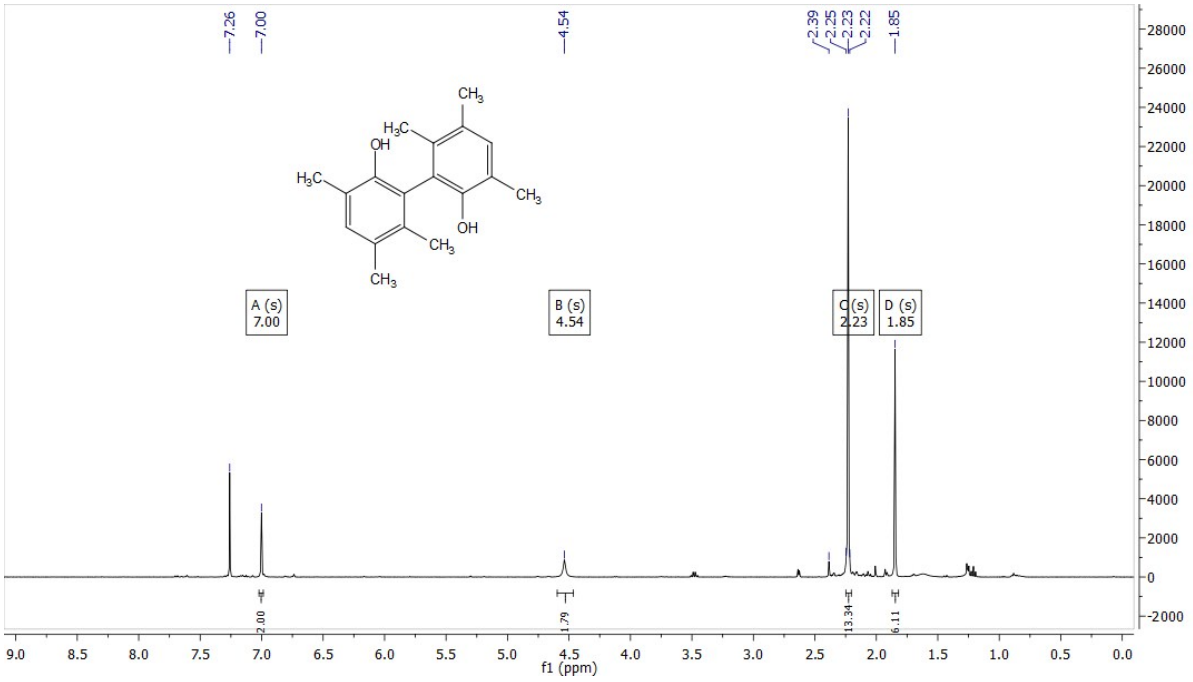


Figure S1. Reaction kinetics of the catalytic oxidation of TMB by **1** at -10 °C. Conversion of TMB (black ●), yield of TMBQ (red ☐) and 2,4,5-TMP (blue ◆) and selectivity for TMBQ (green ■). Reaction conditions: TMB (2 mmo), **1** (0.02 mmol, 1 mol%), H_2O_2 (50 wt% aqueous solution, 2 mmol, 1.0 equiv.), acetonitrile (4 mL).

4. NMR spectra of 3,3’,5,5’,6,6’-hexamethylbiphenyl-2,2’-diol (3,5,6-HMBD)



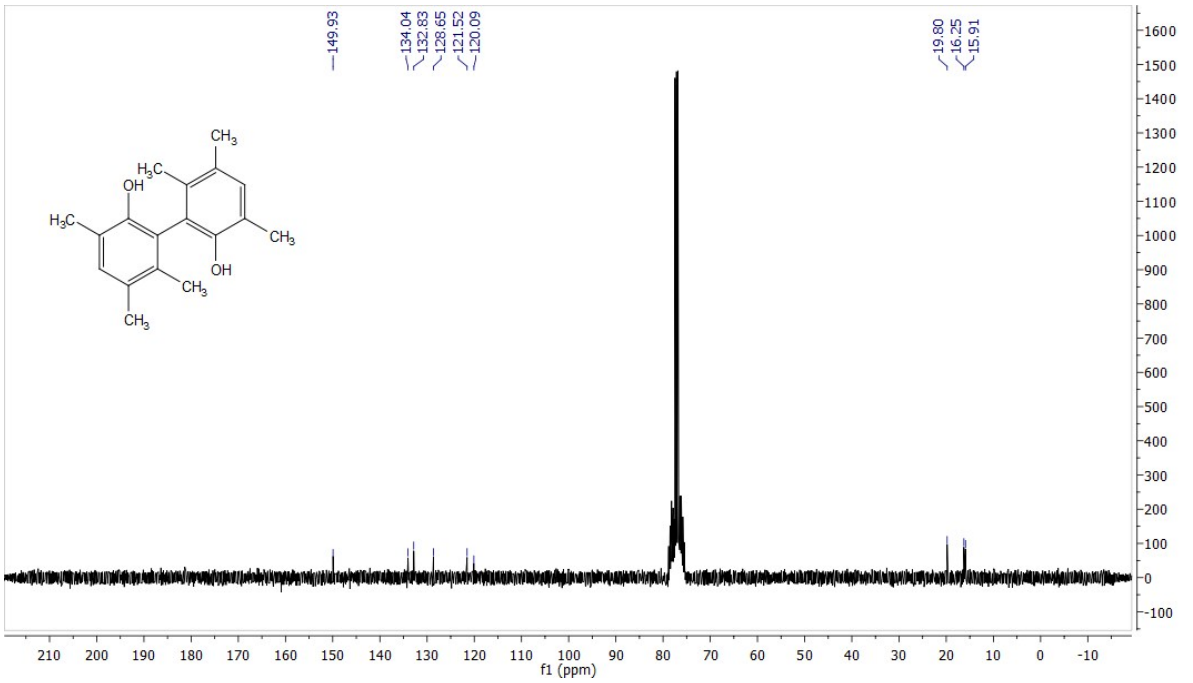


Figure S2. ^{1}H NMR spectrum of 3,3’,5,5’,6,6’-hexamethylbiphenyl-2,2’-diol as received from catalytic oxidation of TMB.

Figure S3. ^{13}C NMR spectrum of 3,3’,5,5’,6,6’-hexamethylbiphenyl-2,2’-diol as received from catalytic oxidation of TMB.